Investigation of Acid-Catalytic Conversion of Carbohydrates in the Presence of Aliphatic Alcohols at Mild Temperatures

V. E. TARABANKO, M. A. SMIRNOVA and M. YU. CHERNYAK

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)

E-mail: veta@icct.ru

Abstract

The processes of fructose and saccharose conversion catalyzed by sodium hydrosulphate and sulphuric acid in biphase water–alcohol (from butanol to octanol) systems as well as in the homogeneous alcoholic media (ethanol, butanol) at 82–102 °C have been studied. It has been demonstrated by GLC-MS and ^{13}C and ^{1}H NMR spectroscopy methods that the main products of conversion of carbohydrates are ethers and esters of 5-hydroxymethyl furfurol and levulic acid, respectively. The total yield of ethers ranges up to 80–90 mol. %. The yield of ethers drops as the concentration of carbohydrates increases. At high concentrations of substrate, the maximum selectivity of acid-catalytic conversion of fructose declines in the following succession: biphase system (water–alcohol) – homogeneous aqueous medium – homogeneous butanol solution. An increase of alcohol molecular weight causes its alkylating capacity in the studied processes to decrease. The results arrived at demonstrate that the combination of alkylation and extraction processes with the removing of the reaction products from the catalytically active aqueous phase in alcohol–water biphase systems makes it possible to increase the yield of the desired products of the process.

INTRODUCTION

Despite a great quantity of data accumulated in the field of chemistry of carbohydrates, the interest to them currently grows, since the sustainable development of the civilization assumes changing over of the raw materials base of chemical industry to recycled vegetative raw material. Acid-catalytic transformations of hexose carbohydrates in an aqueous medium yield levulic acid (LA) and 5-hydroxymethyl furfurol (5-HMF), which is described in detail in the literature [1–6].

The basic difficulties in realization of these processes consist in their low selectivity at the large concentrations of substrate. High values of the LA and 5-HMF yields (about 90 % when recalculated to carbohydrates) are well-known and they are repeatedly described, but the substrate concentration in the reaction mass in these cases does not exceed 0.1 mol/l [3, 7–10].

An increase in the fructose concentration up to 1 M causes the LA yield to decrease to 65 mol. % [8]. In the case of saccharose, the yield of levulic acid drops down to 45 mol. % as the substrate concentration increases to 0.6 mol/l [7]. The principal cause of the low selectivity of dehydration of carbohydrates is, conceivably, instability of 5-HMF under conditions of the reaction and its condensation to form humin substances [8].

The low-temperature (about 100 °C) processes of LA and 5-HMF obtaining from fructose and glucose are generally more selective than the high-temperature ones (160–220 °C) [8, 11]. Accordingly, conversion of fructose in the aqueous medium at 95 °C yields as great as 85 mol percent of LA [6], and a rise in the temperature up to 140–220 °C contributes to a decrease in the yield of the desired products [12, 13]. As the temperature decreases from 240 to 160 °C, the yield of levulic acid from glucose

increases from 29 to 55 mol. % during its conversion in the presence of H_2SO_4 [14].

Possible ways to increase the yields of LA, 5-HMF, and their derivatives consist in using water−organic extractant biphase systems, as well as alkylating agents at the temperatures of about 100 °C. The former allows removing the product from the catalytically active aqueous phase into an organic one and thereby stabilising the product. Application of alkylating agents, on the other hand, may give rise to the more stable products of the process. Aliphatic alcohols combine the properties of both extractants and alkylating agents, which allows the simultaneous use of the both mentioned approaches to increase the efficiency of the processes of acid-catalytic conversion of carbohydrates. The possibility to alkylate 5-HMF with alcohols is mentioned in [12, 13, 15] but this question is not understood in detail.

The solutions of concentrated (1−5 M) inorganic acids that provide a sufficient catalytic activity in the reaction mass are required for dehydration of carbohydrates at low temperatures [3]. This complicates creating biphase systems for such alcohols as butanol or pentanol, because they form homogeneous systems with the concentrated (5−9 M) solutions of H_2SO_4 and HCl [16]. To overcome the difficulty is possible by using the solutions of sodium hydrosulphate and of sulphuric acid as a catalyst [17, 18].

The purpose of the present work is the correlation between the composition and the yields of the products of acid-catalytic conversion of fructose and saccharose in the homogeneous aqueous, aqueous-alcoholic, and alcoholic media and also in water solution−alcohol (from butanol to octanol) biphase systems.

EXPERIMENTAL

Food saccharose and fructose with no additional decontamination, sodium sulphate, sulphuric acid, and ethyl acetate of qualification "kh. ch." (chemically pure), ethanol rectificate, together with butyl, penthyl, isopenthyl, and octyl alcohol (of qualification "kh. ch." and "ch.d.a.") subjected to vacuum distillation were used in this work.

Experiments were conducted in a temperature-controlled flask with stirring. In the case of biphase systems, $Na_2SO_4 \cdot H_2O$ (a mixture of sodium sulphate and sulphuric acid) was used as the catalyst. The heated solutions of the catalyst were mixed with the appropriate amounts of carbohydrates and alcohol and were heated at a temperature of 95 °C for ethyl alcohol and 102 °C for the other alcohols. Fructose conversion in the homogeneous aqueous-alcoholic media was conducted in the presence of H_2SO_4 at a temperature of 82.5 °C for ethyl and 92 °C for butyl alcohols. Concentrated H_2SO_4 (1.8 M) was poured in the small portions into an alcohol solution of fructose that was heated up to the required temperature and the mixture was heated with periodic sampling for carrying out the analysis. The generated samples of the reaction mass, or of the organic phase in the case of the biphase system, of 1 ml in volume were neutralized with saturated $NaHCO_3$ solution to get pH 7, were extracted with ethyl acetate, which was distilled off in the rotational evaporator.

A reaction mass that was generated in the biphase process contained a mixture of butyl levulinate (But-LA) and ether of 5-HMF. To isolate butyl ether of 5-hydroxymethyl furfurol (5-But-OMF), the reaction mass was treated with water solution of alkali and sodium sulphate. Under these conditions, But-LA was subject to hydrolysis, sodium levulinate was transferred to the aqueous phase, and 5-But-OMF was isolated from butanol solution by vacuum distillation.

The generated products were analyzed by the GLC method (a column 2.6 m height, the mass fraction of PEG of 3 % and 1 % of phosphoric acid on INERTON carrier of 0.25−0.30 mm, the internal standard was anthracene) and also in chromato-mass spectrometer Hewlett Packard GCD Plus and in NMR spectrometer Bruker AM-400 (200 MHz) at 25 °C at the Shared-Resource Centre of KSC, Siberian Branch of the Russian Academy of Sciences. NMR spectra were recorded in $CDCl_3$ after solvent stripping. Chemical shift was calculated with reference to $CDCl_3$ signal, using it as the internal standard.

Depending on the conditions of the process and on the nature of alcohol, the

chromatograms of a reaction mixture contained one to four main peaks. Levulic acid and 5-hydroxymethyl furfurol were identified beforehand by NMR and chromato-mass spectrometry methods [17, 19]. Alkyl levulinates and diethyl sulphate were identified on evidence of the database Finigan MAT NIST Library for GCQ/ICIS. The experimental mass spectra of alkyl levulinates were as follows: ethyl levulinate − 144(2), 117(12), 103(1), 99(82), 98(8), 81(5), 74(30), 71(12), 56(7); butyl levulinate − 172(1), 157(3), 130(4), 117(11), 99(100), 98(5), 81(1), 74(20), 71(12), 56(23); pentyl levulinate − 186(2), 157(1), 144(5), 117(16), 99(100), 74(45), 71(15), 56(12); octyl levulinate − 228(2), 157(1), 185(2), 117(29), 99(100), 98(8), 81(2), 74(10), 71(26), 56(10).

^{13}C NMR of 5-But-OMF: δ 14.25 ppm (CH$_3$ of butyl group), 19.62, 32.04 and 65.41 ppm (CH$_2$ groups of butyl radical), 71.50 ppm (CH$_2$ of methoxy group), 111.37 ppm and 122.42 ppm (CH units of the furan ring), 159.37 and 152.94 ppm (carbon atoms of the furan ring with no protons), 178.17 ppm (aldehyde group HC=O).

^{1}HNMR of 5-But-OMF: δ 0.94 ppm (triplet) − CH$_3$ of butyl group, 1.424 ppm (7 lines), 1.624 (5 lines), and 3.552 ppm (triplet) − CH$_2$ groups of butyl radical, 4.557 ppm (singlet) − CH$_2$ of methoxy group, 6.530 and 7.240 ppm (doublets) − CH units of the furan ring, 9.641 ppm (singlet) − aldehyde group HC=O.

RESULTS AND DISCUSSION

Composition of the products of acid-catalytic conversion of carbohydrates in the presence of alcohols

The main products of acid-catalytic conversion of fructose and saccharose in the presence of alcohols, both in single-phase and in biphase systems, represent the well-known esters of levulic acid and ethers of 5-hydroxymethyl furfurol. Previously, these ethers (methyl, ethyl, butyl, and isopenthyl) were synthesized through alkylation of 5-chloromethyl furfurol and were described in the single work [20]. Mass- and NMR spectra of 5-alkoxymethyl furfurols obtained in the present work (Table 1) were not described in the literature.

Spectra of ethers of 5-HMF are analogous to the known spectrum of 5-hydroxymethyl furfurol and show the peaks of molecular ions, which correspond to their molecular mass. The character of molecular splitting under the effect of electronic impact slightly depends on the availability and on the nature of alkyl group and complies with the classical laws of mass spectrometry [21].

Acid-catalytic conversion of carbohydrates in ethanol

Conversion of fructose in the system ethanol−sulphuric acid (1.8 M) with the concentration of water from 0.4 to 1.0 M yields 5-ethoxymethyl furfurol (5-Et-OMF) and ethyl levulinate (Et-LA). The chromatogram of the reaction mass is presented in Fig. 1. Besides the products of transformation of fructose, diethyl sulphate is present in the solution and its concentration is comparable to the concentration of the target products. In the specified reaction system, diethyl sulphate is, obviously, the most active alkylating agent.

The maximum concentration of ethyl ethers of LA and 5-HMF is attained for 30−50 min; their total yield increases from 27 to 82 mol. % as the concentration of substrate is reduced from 0.45 to 0.08 M (Fig. 2).

TABLE 1

Mass spectral characteristics of ethers of 5-HMF

Substance	Peak intensity (m/z)									
5-Et-OMF	154 (30)	−	125 (85)	125 (85)	109 (100)	97 (95)	81 (40)	69 (28)	−	53 (40)
5-But-OMF	182 (8)	183(0.7)	153(10)	125 (4)	109 (100)	97 (75)	81 (30)	69 (7)	57 (8)	53 (20)
5-Pent-OMF	196 (6)	197 (0.5)	167 (5)	125 (3)	109 (100)	97 (68)	81 (25)	69 (11)	−	53 (16)
5-iPent-OMF	196 (8)	−	167 (8)	125 (3)	109 (100)	97 (50)	81 (31)	69 (10)	57 (5)	53 (34)
5-HMF*	126 (50)	127 (4.2)	97 (100)	125 (9)	109 (7)	−	81 (8)	69 (30)	−	53 (17)

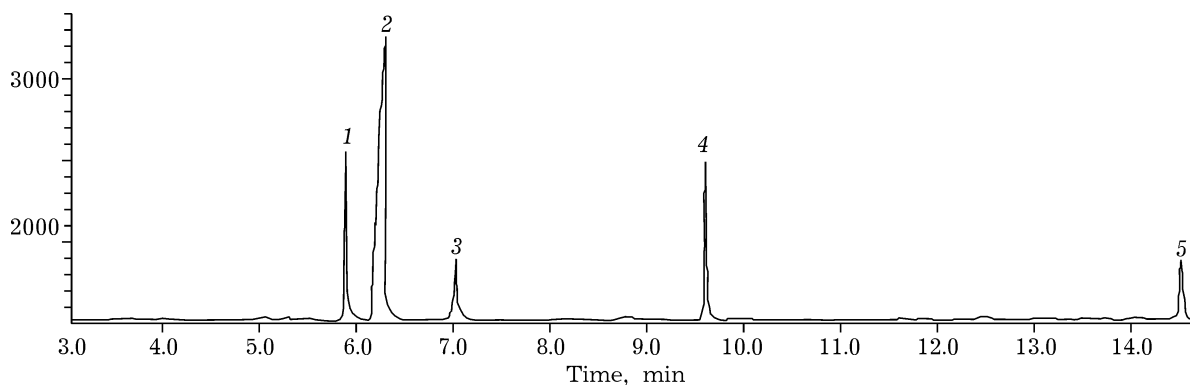*From the database Finigan MAT NIST Library for GCQ/ICIS.

Fig. 1. Chromatogram of the fructose conversion products in ethanol at 82.5 °C: *1* — ethyl levulinate, *2* — 5-ethoxymethyl furfurol, *3* — levulic acid, *4* — diethyl sulphate, *5* — the internal standard.

We failed to realize ethanol−water biphase system: for the reaction mass water−ethanol−saccharose−sodium hydrosulphate, the system composed of aqueous-alcoholic solution of H_2SO_4, carbohydrate, and solid phases of Na_2SO_4 and $Na_2SO_4 \cdot H_2O$ appears to be stable. Conversion of saccharose in such a system at 95 °C yields four basic products, specifically, 5-HMF, LA, and their ethyl ethers. The total yield of these products ranges up to 0.6 mol/ mol of saccharose, and the proportion of ethers among them is of about 70 mol.% (Fig. 3). The maximum yields of the products are attained at the duration of the experiment being 2−3 h.

The ratio between the concentration of ethers and the concentration of associated alcohol and acid is characteristic to a certain degree for kinetics and thermodynamics of 5-HMF and LA alkylation in the system ethanol−water−sulphuric acid. The ratio Et-LA/lA is of about 4−5 and is practically invariant with time. This implies that within the time scale in point, LA alkylation proceeds quickly enough and the resulting ratio is in agreement with the equilibrium one for the solution of this composition. The data acquired allow making a rough estimation of the equilibrium constant of LA alkylation by ethanol:

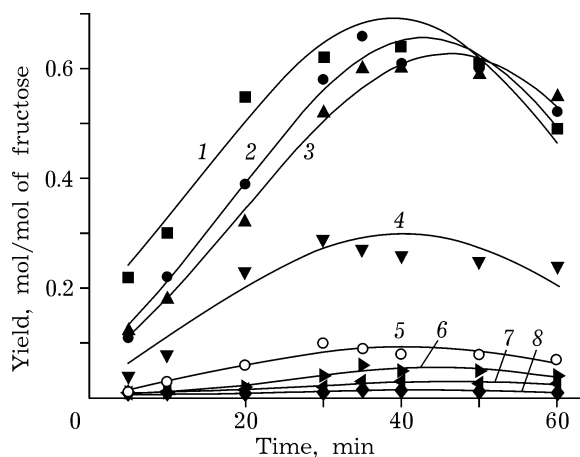$$K = ([\text{Et-LA}] \cdot [H_2O])/([\text{LA}] \cdot [\text{Et-OH}])$$

Fig. 2. Dependence of the yield of 5-ethoxymethyl furfurol (*1−4*) and ethyl levulinate (*5−8*) from fructose on time (82.5 °C, 1.8 M H_2SO_4). C_{fr}, M: 0.08 (*1, 5*), 0.11 (*2, 6*), 0.15 (*3, 7*), 0.28 (*4, 8*).
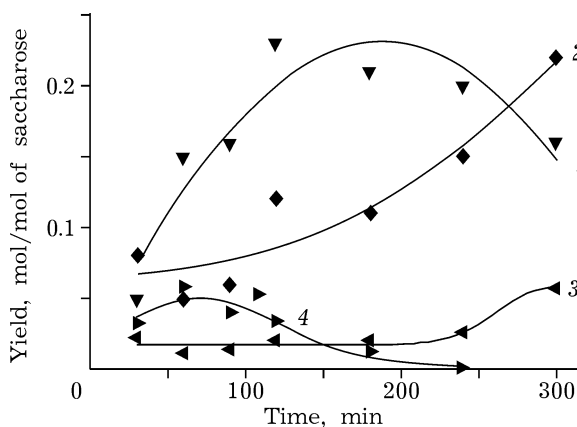

Fig. 3. Dependence of the yield of saccharose dehydration products on time (95 °C, C_{sac} = 0.44 M, 4.6 M $NaHSO_4$+ 0.2 M H_2SO_4, 59 M H_2O): *1* — 5-ethoxy-methyl furfurol, *2* — ethyl levulinate, *3* — levulic acid, *4* — 5-hydroxy-methyl furfurol.
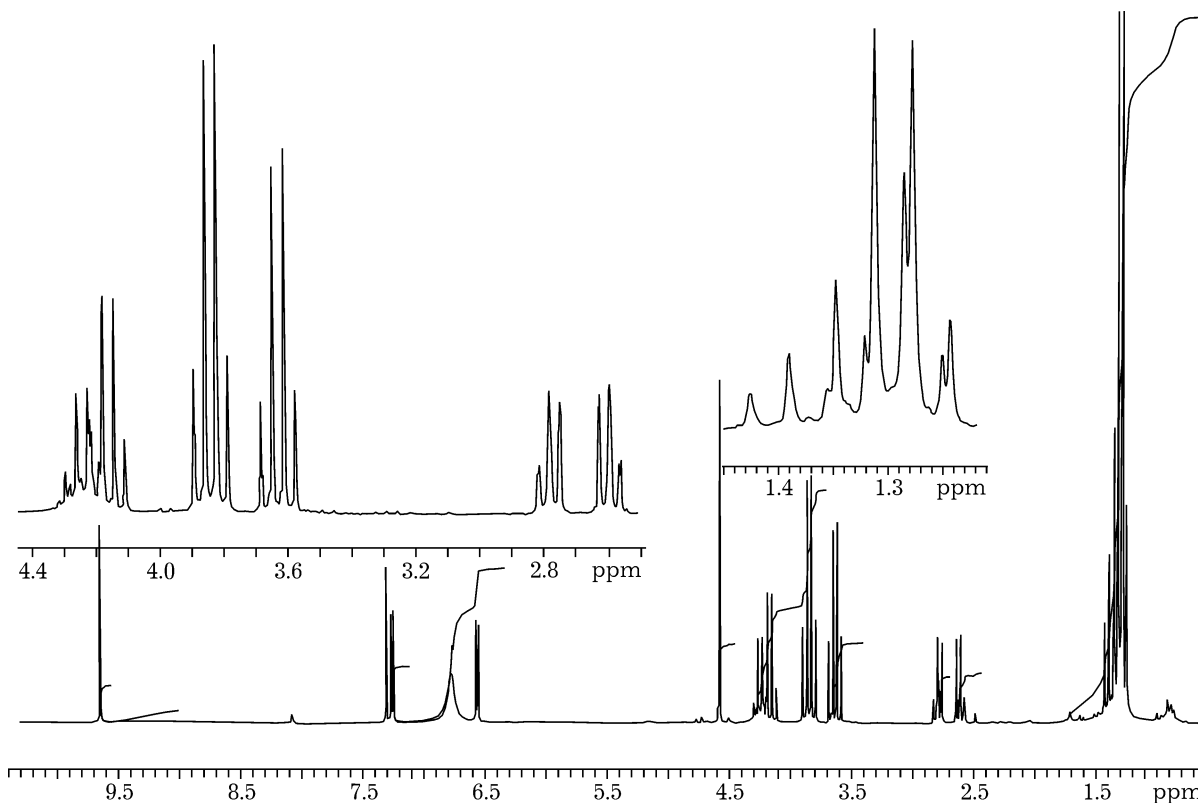
Fig. 4. PMR spectrum of the products of fructose conversion in ethanol in $CDCl_3$ (1.8 M H_2SO_4, 82.5 °C).

The ratio 5-Et-OMF/5-HMF increases with time and reaches the value of 15 and over. Consequently, the process of 5-HMF alkylation proceeds slower than in the case with LA, but the resulting 5-Et-OMF is thermodynamically more stable than ethyl levulinate.

PMR spectrum of the aqueous-alcoholic reaction mass after neutralization and upon removing the solvents and the main part of the deposit of sodium monoethylsulphate is presented in Fig. 4. The signals 9.64 (proton of aldehyde group), doublets 6.53 and 7.24 (protons of the furan ring), and a singlet 4.56 (methoxy group) correspond, obviously, to 5-ethoxymethyl furfurol that was identified by the chromato-mass spectrometry method. Two quartets in the range of values 2.6−2.8 below, apparently, to the methylene groups of acidic part of ethyl levulinate molecule, and a singlet 2.25, to its methyl radical. Present in the spectrum are four quartets in the range of values 3.57−4.27 that correspond, obviously, to the methylene groups of ethyl substituents of 5-ethoxymethyl furfurol and of ethyl levulinate (quartets 4.1−4.3), as well as of diethyl sulphate and monoethylsulphate (3.5−3.9). The absorption range of the protons of methyl groups locates in an interval 1.23−1.44.

Sodium monoethylsulphate is isolated from the reaction mass in the form of crystals upon stripping of solvents. The spectrum of D_2O solution of sodium monoethylsulphate shows two signals (a quartet 3.94 and a triplet 1.22) and does not coincide with the spectrum of ethanol under these conditions (3.68 and 1.12 signals).

Homogeneous acid-catalytic conversion of fructose in butanol

When the process is performed in butanol under homogeneous conditions in much the same manner as in the experiments in ethanol, fructose yields two basic products, namely, 5-But-OMF and But-LA, with the total yield being up to 90 mol. % at the low concentrations of substrate (Fig. 5). With identical concentrations of the catalyst and the substrate, the process in butanol runs much slower than in ethanol: in the latter case, the concentration maximum of the products even
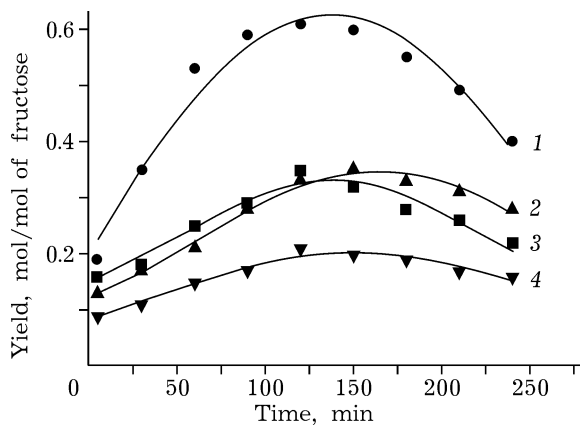
Fig. 5. Dependence of the yield of 5-butoxymethyl furfurol and butyl levulinate from fructose in butanol on time (92 °C, 1.8 M H_2SO_4): *1, 2* − 5-But-OMF, *3, 4* − But-LA; *1, 3* − 0.15 M of fructose; C_{fr}, M: 0.15 (*1, 3*), 0.28 (*2, 4*).

at lower temperature is attained three times quicker than in butanol (see Figs. 2, 5).

Acid-catalytic conversion of saccharose in the butanol-water biphase system

Conversion of saccharose and fructose in the butanol−water biphase system during 200−300 min yields the same main products: butyl ethers of 5-HMF and LA with the total yield

up to 80−90 mol percent (Table 2). Yields of the non-alkylated 5-HMF and LA are at a level of 1 % from the associated ethers despite the aqueous phase existing in the reaction system. So a high alkylation degree is determined, obviously, by the combination of two factors: by the high distribution coefficients of butyl ethers [22] and by the reasonably large equilibrium constants of alkylation (see in the foregoing). The reduced concentration of saccharose from 0.6 to 0.15 M raises the yield of products from 14 to 91 mol. %.

The ratio of concentrations of the main products in homogeneous system 5-But-OMF−But-LA is 2 : 1 unlike the butanol−water biphase system (1.3 : 1 and less). A relatively large proportion of ether in the products of homogeneous process is caused supposedly by the lower activity of water in the homogeneous system as compared to the biphase system. 5-HMF being formed by dehydration of fructose is consumed in accord with two concurrent routes as it interacts with water or alcohol (Scheme 1).

In consequence, the ratio 5-alkoxymethyl furfurol−alkyl levulinate turns out to be the more, the lower is activity of water in the reaction mass.

Obviously, for the analogous reason, the composition of products that are formed in
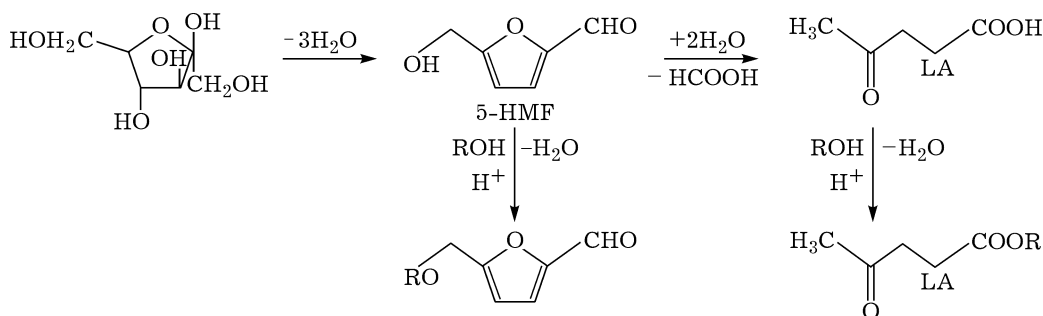
Scheme 1.

TABLE 2

Effect of saccharose concentration in the aqueous phase on the maximum yield and on the concentration of ethers of LA and 5-HMF in the organic phase (102 °C, 4.0 M $NaHSO_4$; the volume ratio of organic to aqueous phase is 2 : 1)

Concentration of saccharose, M	Content of products, g/l		Total yield of ethers, mol/mol of saccharose
	Butyl levulinate	5-butoxymethyl furfurol	
0.146	5.2	6.6	0.91
0.292	6.3	7.6	0.53
0.438	7.4	8.7	0.42
0.584	3.1	4.1	0.14

TABLE 3

Yield of saccharose conversion products in the presence of aliphatic alcohols (102 °C, 4.2 M NaHSO$_4$, 0.44 M of saccharose; the volume ratio of organic to aqueous phase is 2 : 1)

Organic phase	Yield, mol/mol of saccharose	
	Alkyl levulinate	5-Alkoxymethyl furfurol
Butanol	0.20	0.22
Isobutanol	0.24	0.25
Pentanol	0.11	0.16
Isopentanol	0.10	0.14
Octanol	0.06	–

Fig. 6. Dependence of the yield of conversion products on the concentration of fructose in the various media: *1* – water, 1.7 M H$_2$SO$_4$, 2 M NaHSO$_4$, $T = 108$ °C; *2* – butanol, 1.8 M H$_2$SO$_4$, $T = 92$ °C; *3* – biphase medium, butanol–water, 4.2 M NaHSO$_4$; the volume ratio of organic to aqueous phase is 2 : 1.

butanol and ethanol strongly differs too. In ethanol, diethyl sulphate acts as an alkylating reagent. In consequence of this, the rate of alkylation of 5-HMF in the ethanol medium is so great that there is practically no conversion of 5-HMF into levulic acid and 5-Et-OMF appears to be the dominant product.

Effect of the nature of alcohol on the composition and the yield of saccharose conversion products in biphase systems

Yields of alkylation products decrease with the increasing molecular weight of alcohol; the maximum yields of ethers decrease in butanol – octanol series, and ether of 5-HMF is practically not formed with the use of octanol (Table 3). The results arrived at agree well with the data of work [20], where a yield of the desired product in the process of alkylation of 5-chloromethyl furfurol declines from 72 to 31 mol. % in going from methanol to isoamyl alcohol. The decrease in alkylating capacity of alcohols can be also observed, as it was mentioned above, in going from ethanol to butanol.

Comparison of conversion efficiency of carbohydrates in homogeneous and biphase systems

A major aspect of the problem to enhance the efficiency of acid-catalytic conversion of carbohydrates is increasing the absolute concentrations of products in the reaction mass, *i.e.* preserving the high values of selectivity with the increased concentration of substrate in a reactor. It was highlighted previously that at concentrations of carbohydrates of about 0.1 M,
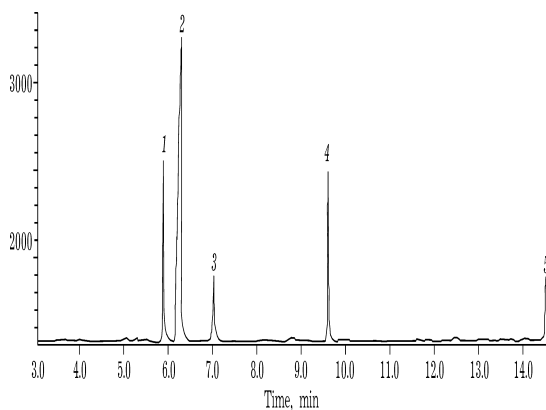
the yields of levulic acid and 5-hydroxymethyl furfurol have been attained in many cases at a level of 90 mol percent; however, with an increase in substrate concentration in the reaction mass, the yield of these products per carbohydrate inevitably lowers.

Figure 6 represents the dependences of the maximum yield of the total of fructose conversion products (LA, 5-HMF, and their ethers) on the concentration of substrate when the process is carried out in the various media. These results have been obtained under rather close conditions (the temperature, activity and nature of a catalyst); therefore, they allow a maximally distinct setting off the effect of phase composition of the reaction system on the yield of products of catalytic conversion.

In homogeneous aqueous and butanol solutions, the high yield of products (60–90 %) per substrate) is observed at the concentrations of fructose less than 0.2 M. However, as C_{fr} increases to 0.8 M, they decrease by a factor of 4–5. In the biphase system, the decrease in a yield of products below 80 % is observed at $C_{fr} > 1$ M. At the concentration of fructose of 0.8 M, acid-catalytic conversion in the biphase system yields a 6–8 times greater yield of products as compared to single-phase homogeneous solutions.

Those significant distinctions in the efficiency of the processes are caused, apparently, by the separation of the products (the organic

Yield of the products up to 83−90 mol. %	Organic		Distribution coefficient
	phase (butanol)		of the alkylated products
	The products:		$k = 70-100$
	But-LA		
	5-But-OMF		
Distribution coefficient of the catalyst $k = 0.03-0.05$	Aqueous solution of fructose and $NaHSO_4$ catalyst The products: 5-HMF, LA		Distribution coefficient of the products $k = 2-4$

Scheme 2.

phase) from the catalyst and substrate (the aqueous phase) in the course of the reaction (Scheme 2).

Contrary to H_2SO_4, sodium hydrosulphate produces a stable biphase system, the distribution coefficient of the catalyst being below 0.03−0.05 even for its concentrated solutions in the aqueous phase. The distribution coefficient of levulic acid and 5-hydroxymethyl furfurol that are obtained in a homogeneous single-phase system is 2−4; however, resulting from their alkylation, the distribution coefficients of the obtained products increase up to 70−100. Such a ratio of distribution coefficients of the catalyst and the products of the process ensures their effective separation.

Thus, removal of the reaction products from the active aqueous phase through combination of the processes of alkylation and extraction makes it possible to increase their yield at high concentrations of fructose, and this approach is most effective as compared to those described in the literature.

Acknowledgements

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